

Supporting Information:

Structural Elucidation of *cis/trans* DicaFFEoylquinic Acid Photoisomerization Using Ion Mobility Spectrometry-Mass Spectrometry

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Time-dependent Photoisomerization

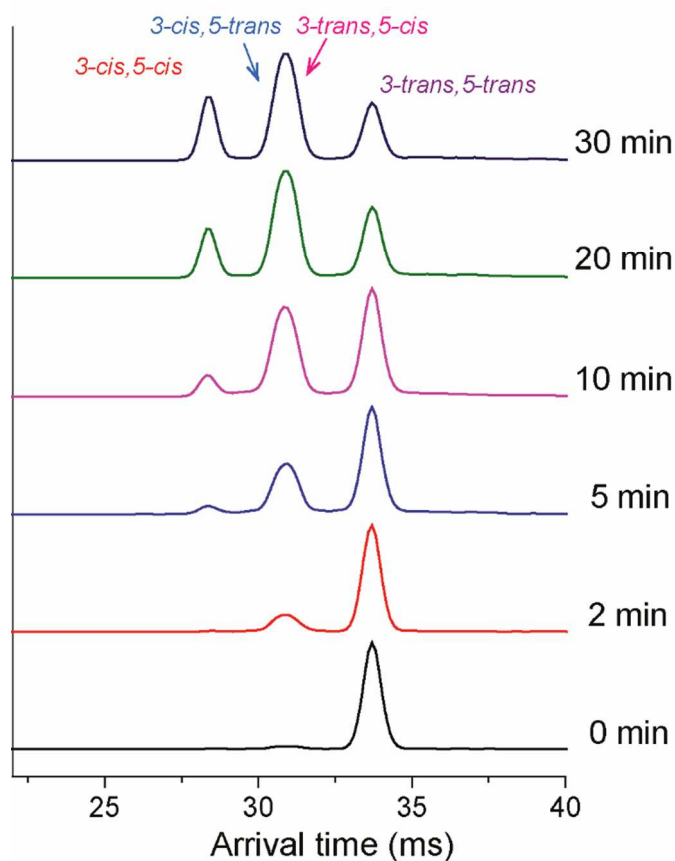


Figure S1. Time-dependent photoisomerization of 3,5-diCQA was monitored with IMS-MS following UV irradiation for 2, 5, 10, 20 and 30 minutes. Without UV irradiation, 3,5-diCQA exists in the *trans,trans* conformation. After 2 minutes' UV irradiation, the 3-*cis*,5-*trans* and 3-*trans*,5-*cis* conformers were observed evenly but no 3-*cis*,5-*cis* conformer. However as the time of UV irradiation was increased, the *cis,cis* conformation started to appear.

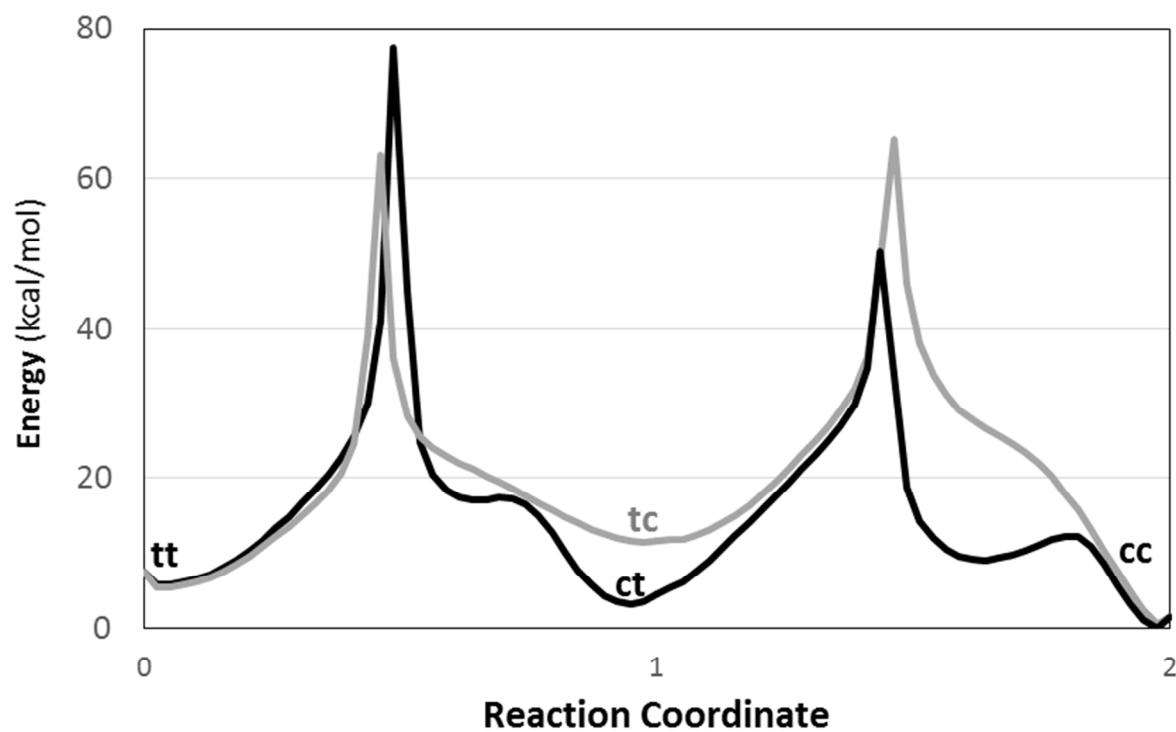
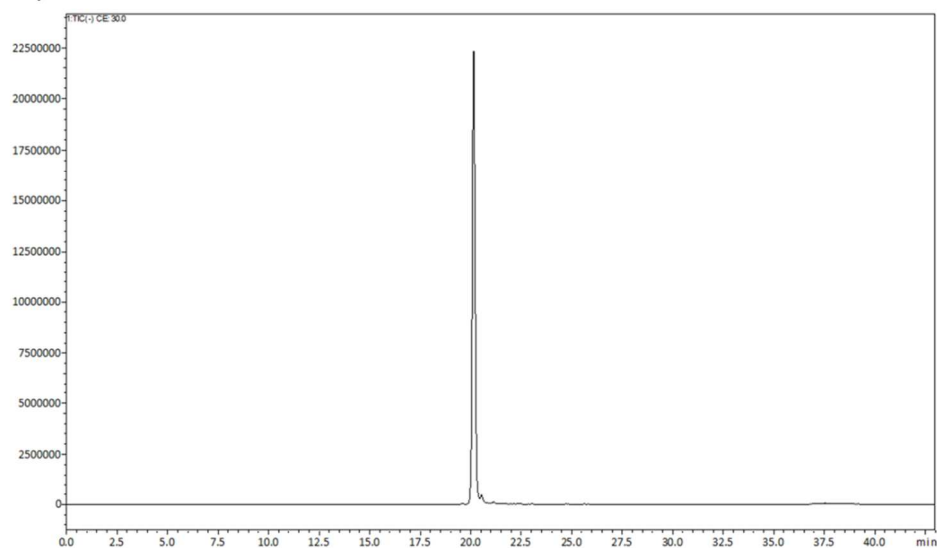


Figure S2. The minimum-energy path from 3-*trans*,5-*trans* diCQA (tt) through 3-*trans*,5-*cis* diCQA (tc, grey line) and 3-*cis*,5-*trans* diCQA (ct, black line) to 3-*cis*,5-*cis* diCQA (cc), using the “string method” as implemented in NWChem.

A) Before UV irradiation



B) After 3 hours' UV irradiation

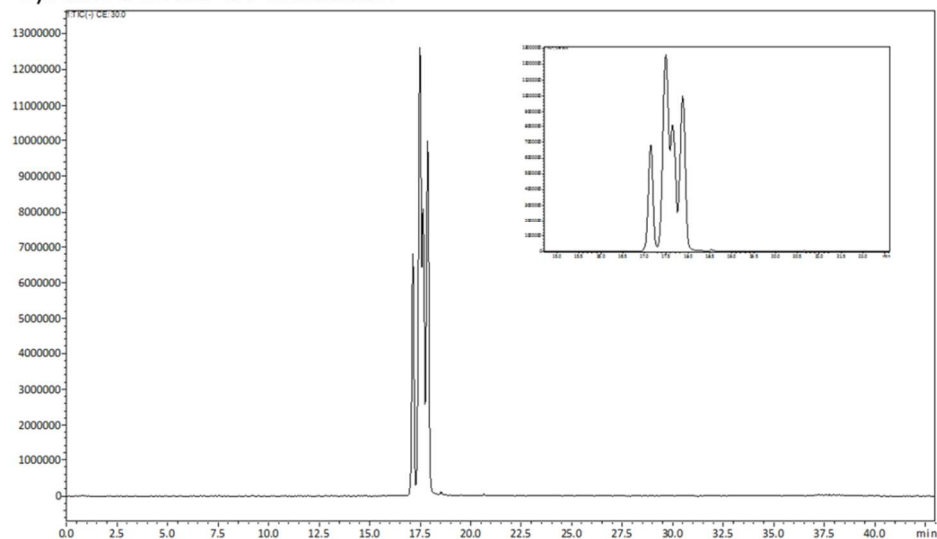


Figure S3. LC chromatograms for 3,5-diCQA, A) before and B) after UV irradiation. The products of UV irradiation were analyzed by liquid chromatography-mass spectrometry and no other species were observed other than those peaks corresponding to *cis,cis*; *cis,trans*; *trans,cis*; and *trans,trans* 3,5-diCQA isomers.

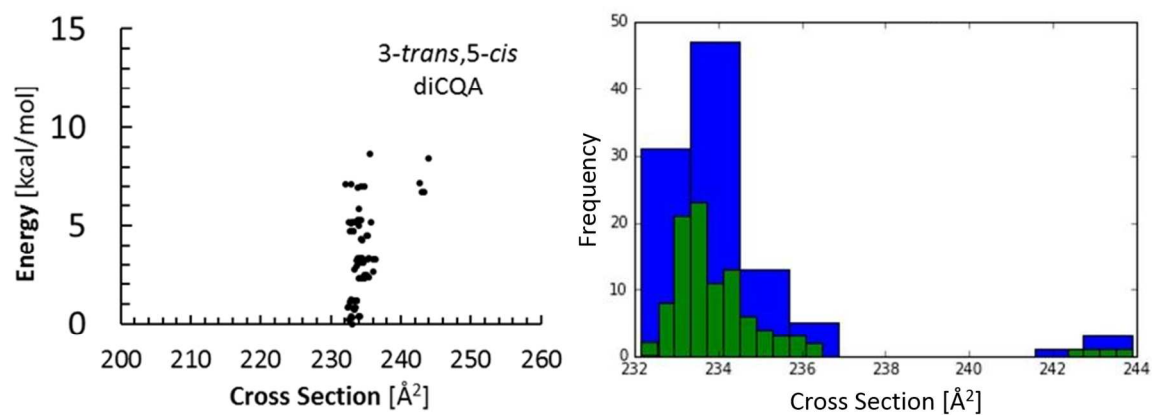


Figure S4. An example scatter plot and cluster diagram for 3-*trans*,5-*cis* diCQA. The scatter plot illustrates the relative energies for the 100 3-*trans*,5-*cis* diCQA structures from the *ab initio* calculations versus the collision cross sections determined with MOBCAL. The cluster diagram shows the frequency of CCS for each conformer in the scatter plot with both coarse (blue) and fine (green) binning.